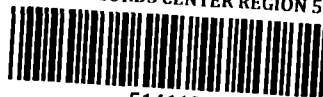


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Wood Preservatives: Their Depletion as Fungicides and Fate in the Environment



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WOOD PRESERVATIVES: THEIR DEPLETION AS FUNGICIDES AND FATE IN THE ENVIRONMENT

by

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Résumé en français

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ABSTRACT

Wood preservatives are highly toxic chemicals and thus are potentially hazardous to humans, domestic animals, and other forms of life. Up to now, wood preservatives have not polluted the environment, mainly because they have been handled with care and usage has been relatively small. This literature review was undertaken at the request of industry to help gain perspective on the fate of preservatives in the environment. Biological and other factors affecting the permanence, depletion, and breakdown of creosote, chlorinated organic toxicants, and inorganic salt preservatives are discussed. Outlines of the basic mechanisms by which microorganisms break down aliphatic, aromatic, and inorganic molecules are included, and brief reference is made to photodegradation of toxicants. Possible directions for the future development of preservatives that have little if any potential to damage the environment are also indicated. Environmental problems from wood preservative usage are not expected in the immediate future apart from those possibly created by the release of effluents from treating plants. Should difficulty develop in this area, remedial technology is in most cases available.

RÉSUMÉ

Les fongicides du bois sont des produits chimiques très toxiques et, par conséquent, potentiellement dangereux pour l'homme, les animaux domestiques et autres formes de vie. A ce jour, c'est surtout à cause d'une utilisation prudente et relativement minime qu'ils n'ont pas pollué l'environnement. On a compilé la présente documentation à la demande des industriels, pour les aider à obtenir une perspective des conséquences écologiques de l'utilisation de ces fongicides. L'auteur discute des facteurs biologiques et autres qui affectent la durabilité, l'épuisement et la décomposition de la créosote, des matières toxiques organiques et chlorées et des fongicides sous forme de sel inorganique. On donne un aperçu des mécanismes de base responsables de la décomposition par les micro-organismes des molécules aliphatiques, aromatiques et inorganiques. On mentionne brièvement la photodégradation des toxiques. On indique également les possibilités d'avenir quant au développement de fongicides qui seraient peu, ou pas, nuisibles à l'environnement. Sauf pour les problèmes que pourrait créer l'écoulement des effluents des usines de traitement, on ne s'attend pas, dans l'avenir immédiat, à des problèmes écologiques causés par ces fongicides. Si de telles difficultés surviennent, on peut avoir recours, dans la plupart des cas, à une technologie de prévention.

CONTENTS

	<u>Page</u>
INTRODUCTION.....	1
WOOD PRESERVATIVE USAGE.....	1
DEPLETION OF WOOD PRESERVATIVES AND OTHER TOXIC SUBSTANCES IN GENERAL.....	2
Detoxification of Aliphatics.....	4
Detoxification of Aromatics.....	5
CREOSOTE.....	6
Microbiological Breakdown.....	7
Detoxification Mechanisms.....	8
Photochemical Breakdown.....	8
Permanence.....	9
CHLORINATED TOXICANTS AND PENTACHLOROPHENOL.....	10
Microbiological Breakdown.....	10
Detoxification Mechanisms.....	11
Photochemical Breakdown.....	14
Permanence.....	15
METALLORGANIC AND INORGANIC WOOD PRESERVATIVES.....	15
Microbiological Breakdown.....	16
Detoxification Mechanisms.....	17
Permanence.....	19
ENVIRONMENTAL HAZARDS OF TOXIC CHEMICALS AND WOOD PRESERVATIVES.....	20
PROSPECTS FOR NEW WOOD PRESERVATIVES.....	22
ACKNOWLEDGMENTS.....	24
REFERENCES.....	25

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WOOD PRESERVATIVES: THEIR DEPLETION AS FUNGICIDES AND FATE IN THE ENVIRONMENT

INTRODUCTION

Man has become increasingly aware of his immediate and global environment and has already raised strong objection to the widespread pollution of inland waters, air, soil, and the oceans. Our rapid development, population explosion, increased technology, and industrialization, and the extensive use of synthetic chemicals in industry, agriculture, and the home, have all polluted the environment. Approximately 20 million tons (18.1 million tonnes) of manufactured chemicals enter the environment annually (Lliff 1972). About 50% are common solvents, 7.5% are active detergents, 5% are organic pesticides that kill fungi and insects as do wood preservatives, 5% are gaseous chemicals, and the remainder are miscellaneous organic chemicals including 2 to 5 million tons (1.8 to 4.5 million tonnes) of lubricating oils.

Wood preservatives are a group of toxic materials that in the future may threaten the environment. Immediate hazards from wood preservatives exist only at manufacturing and treating-plant sites, perhaps causing local problems as plant effluents find their way into soil and water nearby (Thompson and Dust 1971). A far greater threat exists from the pesticide industry since the amounts used therein and the areas treated are many times greater than in the wood preservation industry. Nevertheless, wood preservation is constantly expanding by way of new products and new uses. For example, the employment of wooden foundations for housing has gone beyond the experimental stage, and legislation is passed and standards are being set to allow their use. Whole communities with wooden foundations are foreseen, placing untold quantities of preservative-treated wood in the soil ecosystem with some hazard to humans and domestic animals. The wood preservation industry wants to be aware of the pollution problems arising from the extensive use of preservatives (Sedziak and Unligil 1973). To avoid pollution from wood preservation, manufacturers and users of preservatives require knowledge of the toxicity, leachability, persistence, and ultimate fate of their preservatives. To help, and at the request of the industry, the literature has been surveyed.

WOOD PRESERVATIVE USAGE

Wood preservative usage has increased steadily, particularly since 1969. Copper-chrome-arsenate (CCA) has found increasing popularity as a preservative for all kinds of timber structures. Pentachlorophenol (PCP) with petroleum as a carrier has been used increasingly for the treatment of poles. Statistics compiled by the AWWPA (American Wood Preservers' Association) for 1971 (Gill and Phelps 1972) list the use of preservatives in the USA as

219 million gallons (829 million liters) of liquid, 45 million pounds (20 million kilograms) of solid and 18 million pounds (8 million kilograms) of fire retardant. About 268.6 million cubic feet (8 million cubic meters) of timber was preserved in some 390 treating plants. Poles, crossties, lumber and timbers, fence posts, pilings, switch ties, and crossarms were impregnated. The use of preservative for plywood increased 15% during 1970 and 1971, a significant rise. Similarly, the use of fixed salt preservatives was up 15% over the same period. Total preservative usage is said to increase 3% a year. Statistics for the treatment of wood in Canada are not readily available, but some 49 treating plants are operative. In comparison with the toxic chemicals utilized by the pesticide industry the quantities required for the wood preservation industry are perhaps small, but the chemicals employed are equally hazardous.

DEPLETION OF WOOD PRESERVATIVES AND OTHER TOXIC SUBSTANCES IN GENERAL

Current wood preservation practice makes use of tar oils such as liquid creosote (either alone or in petroleum), organic solids like PCP, chlorinated naphthalenes, metallic naphthalenes, and water-borne preservatives, containing salts of Cu, Cr, As, and Zn, and Na and K salts of PCP. Dieldrin and lindane, which are insecticides, have also been used for the preservation of wood against insect attack.

Preserved wood is used in contact with soil, both above ground and under water. Preservative action is thought to begin with the movement of toxic material from the preserved timber to the immediate environment, i.e. to the soil or water surrounding the installation. A zone of defense against invading organisms is thus set up, but the situation is not static and the same toxic material is leached away in time to be replaced by more from the preserved timber (Petrenko 1969). A leaching, or loss of preservative to the environment, may therefore be the mechanism operative for the prevention of decay. However, treatment with and selection of preservatives have been directed to attaining maximum fixation of the preservative in the wood for long-term protection. The type of preservative used, the soil and moisture condition, and the microbiological complexity of the immediate ecosystem together regulate the performance of a preservative, its permanence, or its degradation and subsequent release and movement from the treated material. Once preservatives enter the environment beyond the service area they become pollutants.

Alexander (1971), a leading authority on toxicants and their behavior in the environment, considers that most naturally occurring organic compounds can be degraded by one or another microbial species, given proper conditions of exposure. Evidence is accumulating that detoxification and breakdown occur through metabolic and cometabolic processes involving oxidation, reduction, hydrolysis, dehalogenation, conjugation, and hydroxylation reactions. Physicochemical and photodegradative processes in the environment also contribute. In a later paper Alexander (1973) is careful to point out that some natural materials, such as paleobiochemicals, carbon components of humus, and surfaces of resting stages of certain

bacteria and fungi, endure. In the last 30 years the chemical industry has given to man extremely toxic chemicals not synthesized by natural biochemical processes and which probably degrade at best extremely slowly when exposed to the environment. Some chemical substances employed as wood preservatives may fall into this category and therefore may be "recalcitrant" or resistant to degradation when deposited in the environmental ecosystem (Alexander 1965, 1969). Biodegradable material is usually metabolized so that the degradation products ultimately become incorporated into the major cycles, which help to establish life processes. Several such cycles are operative, namely those for carbon, nitrogen, phosphorus, and sulfur. The most extensive of these is the carbon cycle. Terrestrial and aquatic carbonaceous material is broken down ultimately to carbon dioxide and water by the action of microorganisms. The carbon dioxide formed is assimilated by living plants during growth. Plant material as a food source for many life forms is metabolized and respired and carbon dioxide and water are again formed, and the cycle continues. Similarly, conversion cycles for nitrogen, phosphorus, and sulfur can be traced (Alexander 1971) such that in total a balance of elemental materials is maintained and no one substance piles up to pollute the environment.

It has been demonstrated that many organic substances are not degraded completely to such simple molecules as CO_2 and H_2O and that yet specific organisms can modify the molecule (Menzie 1972). Many toxic substances are detoxified in this way. A simple change of some active functional group by microbiological activity can so alter a molecule that the toxicity becomes less to the organism effecting the reaction. However, toxicity may increase for other organisms endeavoring to become established.

Toxicants can be affected by solubility, absorption (by organic matter), vapor pressure, temperature and other physicochemical phenomena. Leutritz (1965) considered that these factors were the most important with respect to depletion of PCP and that biological degradation was not well proven. After tests of posts and feeder strips treated with PCP and buried in sterile and nonsterile soil, he concluded that loss of PCP was caused by bleeding of the carrier with PCP dissolved in it. An investigation by Unligil (1968) also supported physical loss of preservative: he found that wood blocks impregnated with PCP but without carrier were depleted of PCP by sterilization (volatilization) and (after an incubation period in sterile soil-block culture jars) were depleted by evaporation and leaching. In addition microbiological degradation was shown to occur. Goring (1967) has emphasized the physicochemical factors causing depletion of toxicants but at the same time has recognized that degradation is caused by microorganisms. After the accumulation of many more data he expects to give it mathematical expression to predict the permanence of toxicants in service. He has stressed that we need to know, in addition to existing data, the organic matter-to-water ratios, the rate of decomposition of a compound in soil, and the concentration and times necessary to give a certain level of kill of the more important pathogens (see Munnecke 1972). These data are unknown. All investigations are complicated by the soil, an extremely complex physical-chemical-biological system. Primarily involved are sorption phenomena, solid-liquid interface activity, soil moisture as it affects the

mobility of toxicants, soil aeration, and oxidative effects (Munnecke 1972, Garraway 1972). In addition, light affects many toxicants; this form of degradation is not generally recognized, but there has been some study for PCP formulations.

DETOXIFICATION OF ALIPHATICS

Aliphatic hydrocarbons and various substituted derivatives thereof are important as carriers for preservatives in wood treatment and also comprise certain fractions of the coal tar preservative creosote. Many of these substances are biodegradable, but the behavior of some may pollute the environment.

The mechanisms by which aliphatic substances are degraded have been only partially established. Beta oxidation plays a major role. Methane, a gaseous alkane, is oxidized via methanol to formaldehyde to formate by select organisms (Traxler and Flannery 1968). Other gaseous alkanes (C_2-C_5) are detoxified by two main routes: (1) alcohol to aldehyde to acid and (2) via methyl ketone formation. Intermediate alkanes (C_6-C_{12}) are oxidized at the C_1 atom and the corresponding acid is formed; betaoxidation follows, reducing the molecule to smaller chain lengths. Longer chains ($C_{12}-C_n$) also undergo terminal C_1 oxidation to form the fatty acid, but as a minor mechanism dicarboxylic acid formation can occur. Regardless of the initial route, beta-oxidation takes place to reduce chain length. Three pathways, therefore, are apparent - (1) alcohol to aldehyde to acid, (2) methyl ketone formation, and (3) diterminal reaction (alpha-omega oxidation) - and for long-chain molecules all are followed by beta oxidation and cleavage to shorter chains.

Circumstances influence biodegradation. For example, the breakdown of n-alkanes may be stimulated or inhibited by the simultaneous presence of alkylbenzenes (Traxler and Bernard 1969). The effect is principally a function of the number of methyl substitutions to the benzene ring, and the suggestion is that cell permeability of the participating microorganisms is affected. The chemical environment of aliphatics in contact with the ecosystem would therefore affect their fate in the environment.

Recalcitrance or resistance to degradation by aliphatics is principally affected by their substituents. For example, two protons are required for both the alpha and the beta carbon atoms if beta oxidation is to occur with fatty acids, and any substitution here results in highly refractory substances (Alexander 1973). Both multiple branching and the presence of two methyl groups on single carbon atoms also create obstacles to biodegradative cleavage. Similarly the presence of a quaternary carbon atom near the end of an alkyl chain deters beta oxidation. There is evidence that chain cleavage ceases as the branched site is approached, since the products of reaction still contain the substituted structure. Halogenation of the alpha carbon has been found to deter oxidation, whereas omega halogenation does not. From the data at present available few generalizations relating structure to biodegradability can be drawn.

DETOXIFICATION OF AROMATICS

Much of the available information on the biodegradation of aromatic toxic substances is from studies of the simpler derivatives of benzene. From these a general scheme outlining the biochemical pathway for ring cleavage and the assimilation of substances into the cycles of general metabolism has been elucidated. Complete degradation of polychlorinated aromatic substances such as PCP by biodegradation will probably be found closely allied to the known pattern irrespective of the initial degradative mechanisms that may be involved. Most such reactions are enzyme-catalyzed. Phenol oxidases, i.e. laccases, tyrosinases, and peroxidases, are widely distributed in plants, bacteria, and fungi including the wood-rot fungi and are known participants. According to Brown (1967) the most important fact about phenol oxidases known with reasonable certainty is that these enzymes catalyze the production of aryloxy radicals from the phenol substrates. The reactions that follow, such as hydroxylation, quinone formation, and oxidative coupling, stem from the chemical reactivity of these aryloxy radicals. Ring-cleavage reactions are best understood from investigations in which bacteria, mostly *Pseudomonas* species, were used as the degradative agents. The reaction sequences involved have recently been reviewed by Ornston (1971), and his reaction schemes are shown in Fig. 1. Catechol and protocatechuic acid are the central metabolites around which aromatic compounds are broken down. Some

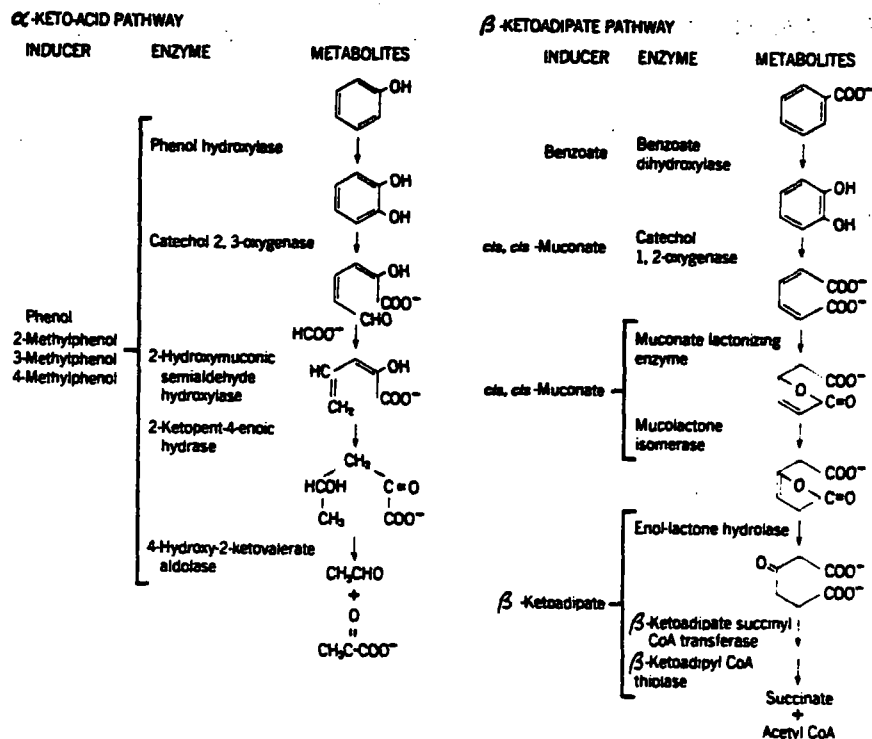
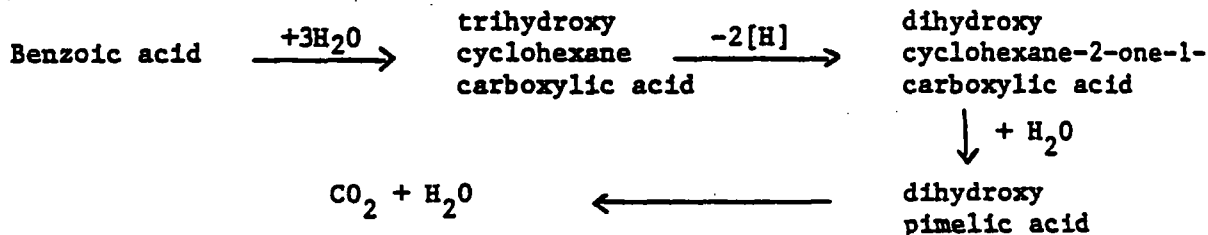


Figure 1. Regulation of the α-keto-acid and the β-ketoadipate pathways in the single strain of *Pseudomonas putida*. (Based on Orniston 1971, Fig. 16.)

pseudomonads cleave protocatechuate and catechol by splitting the ring on one side of, rather than between, the neighboring hydroxyl groups. This is termed metaring cleavage and produces α -keto acid as an intermediate. Cleavage of the ring between hydroxyl groups is termed ortho-ring cleavage: this leads to the production of β -ketoadipate as intermediate. The type of cleavage obtained is affected by the substitutions on the ring system. It is suggested that ring structures bearing electron-withdrawing groups, for example protocatechuate and cinnamic acid, suffer biodegradation by the β -ketoadipate pathway and that ring structures bearing electron-donating alkyl groups result in enzyme induction leading to the α -keto-acid biodegradative pathway (Seidman et al. 1969). Thus phenol and its methyl derivatives induce all the enzymes of the α -keto-acid pathway. On the other hand, benzoate is restricted to the enzyme complex that mediates its conversion to catechol to *cis*, *cis*-muconate through the β -ketoadipate pathway. The ultimate reaction products - succinate, acetyl CoA, acetaldehyde, and pyruvic acid - are free to enter the citric acid metabolic cycle and are finally dissipated as carbon dioxide and water.

A metabolic pathway distinctly different from the aerobic pathways already noted is emerging for the anaerobic degradation of aromatic substances. Apparently the aromatic ring is reduced to a cyclohexane derivative and thus the mechanism has been termed a "reductive" pathway (Dutton and Evans 1968, Guyer and Hegeman 1969). Taylor et al. (1970) have proposed, as did Stanier (1948), that water be added to the aromatic ring as follows:



A recent paper by Williams and Evans (1973) questions this concept but considers it to be an interesting explanation. They identified *trans*-2-hydroxycyclohexane-1-carboxylate and two other as yet unidentified compounds as being derived by the anaerobic reductive pathway for *Pseudomonas stutzeri* acting upon benzoate.

CREOSOTE

Good timber preservation practice under most circumstances requires that sapwood be protected against decay-causing organisms, whereas the heartwood of many species contains toxic substances that are natural inhibitors to wood-rot microorganisms. One of the oldest wood-decay preventives is coal-tar creosote. Creosote is a very complex chemical mixture, being a distillate of coal tar from the 175-200°C fraction up to and including the 400-450°C fraction; it is characterized as high boiling if above or low boiling if below 235°C. Roche (1952) found more than 160 substances in creosote and most of them are known to be toxic to microorganisms. Creosote

comprises:

1. tar acids - phenols, cresols, xylenols, and naphthols (all toxic to wood-rot fungi),
2. tar bases - pyridines, quinolines, and acridines (most are toxic to wood-rot fungi),
3. hydrocarbons (neutral oils) - naphthalene, anthracene, benzene, toluene, xylene, acenaphthene, phenanthrene, and fluorene (some are toxic to wood-rot fungi),

the largest fraction being the hydrocarbons. In spite of the highly toxic nature of creosote, treated lumber can be degraded and the toxic materials depleted; consequently structures built from it may fail. However, with proper application and care in handling, creosoted timber has given excellent service.

MICROBIOLOGICAL BREAKDOWN

Some detoxification of such a complex mixture as creosote is to be expected, for it is generally conceded that natural habitats abound with microorganisms capable of degrading organic substances. Even relatively early investigators (Gray and Thornton 1928) showed that soil bacteria could decompose aromatic compounds such as phenol, creosol, naphthalene, toluene, and many other substances. Similarly, a later study showed that marine bacterial species were capable of oxidizing many aliphatic and cyclic hydrocarbons including kerosene, paraffin, penta-, hexa-, and deca-alkanes, benzene, anthracene, and naphthalene (Zobel et al. 1943).

It is not surprising then that Christensen et al. (1942) observed *Hiromodendrum resinae* to be closely associated with creosote-treated timber. Marsden (1954) suggested that this organism reduced the toxicity of the creosote since it was also found to metabolize creosote, which acted as a sole carbon source. Similarly, from pilings in a marine environment, O'Neill et al. (1961) isolated a creosote-tolerant bacterium, *Pseudomonas creosotensis*, capable of growth in a medium containing up to 1% creosote in the presence of other carbon sources. Later Drisko and O'Neill (1966), using this organism mixed with others, showed that naphthalene and phenanthrene, two toxic constituents of creosote, were changed chemically through microbial action. A chemical change caused by *P. creosotensis* was shown by spectrophotometric analysis to occur between the creosote of the interior and exterior parts of pilings. Apparently the outer material contained greater amounts of hydrocarbon groupings and oxidation products than the inner material (Drisko 1963). About the same time Ueyama and Akai (1965) cultured *H. resinae* in creosote concentrations as high as 16%. Naphthalene and phenanthrene were prominent in the high-boiling creosote fraction used.

Cladosporium resinae (synonymous with *H. resinae*) was isolated in pure culture by Parbery (1967), who used a technique he developed employing

creosoted match sticks. The organism was termed the "kerosene fungus" and has been found widespread in nature as, for example, in the resins of pine and cedars, in storage tanks holding aviation fuels, and where coal-tar products occur (Parbery 1969). Parbery (1972) has suggested that factors other than genetic ones may induce certain changes in *C. resinae* and believe that certain "ecotypes" exist that have been selected to grow at various points down the soil profile. The ecotypes from deep in the soil appear to differ from those at the surface. In a survey of a coal measure in South Wales *C. resinae* was detected along with several other species and all were shown to be capable of metabolizing various hydrocarbons (Jones and Edinborough 1968). Apparently more of these organisms could utilize the long chain than the short chain aliphatic hydrocarbons, aromatics, or alicyclic hydrocarbons. This was in accord with the findings of Teh and Lee (1973). Using four different isolates of *C. resinae*, they observed that n-alkanes ranging from n-nonane to n-octadecane were metabolized and that C₁₄ to C₁₈ material supported the growth best. Shorter chain alkanes, including gasoline containing short chain alkanes, were not utilized. Similar results were observed by Cofone et al. (1973) when investigating the utilization of a wide range of hydrocarbons by *C. resinae*. In addition benzene and substituted benzene (methyl and propyl) were metabolized, albeit slowly. The occurrence of *C. resinae* within creosoted timbers and in soil has recently been reviewed (Sheridan et al. 1972). In some proving ground tests with various preservatives including an anthracene oil type, Petrenko (1969) was able to show various genera including *Pseudomonas*, *Alternaria*, *Pullularia* and *Montospora* to be associated with preserved wood. Increased retention of preservative did not change the type organisms found. From these data and other literature not cited it can be concluded that coal-tar creosote can be expected to undergo some sort of attack by select microorganisms when placed in service whether it be submerged in soil or water.

DETOXIFICATION MECHANISMS

The mechanisms for creosote detoxification have not been studied. Creosote preparations normally contain a high percentage of aromatic material and this contributes to their principal toxicity. Detoxification of this material by microbiological systems would be expected to follow the pattern already discussed for aromatics (Ornston 1971), at least with respect to final-product formation, which begins with ring cleavage and ends with complete oxidation to carbon dioxide and water. Initial detoxification reactions proceeding to ring cleavage would probably be influenced by the particular ring system and substituted groups involved and by synergistic interaction between the host of heterogeneous chemical substances peculiar to creosote.

PHOTOCHEMICAL BREAKDOWN

Photochemical decomposition of creosote has not been reported in the literature. However, creosote-treated material has often shown

weathering effects, and this in part must be attributed to photochemical oxidation. A complex material like creosote would be expected to contain photolytes mainly because of its aromatic content. Photooxidation has been well established for similar substances such as phenol, cresols, and dihydroxybenzenes (Joschek and Miller 1966) as well as for most compounds in petroleum and cosolvents (Arsenault 1973). Photooxidation takes place when ultraviolet radiation apparently effects higher electronic excitation levels in molecules, and this leads to the formation of singlet and triplet states. This in turn results in free radical formation, thus initiating photolysis and cross linking of susceptible molecules (De Mayo 1971).

Possibly photochemical reactions are of little consequence for creosote and other preservative-treated structures, since the wood substance protects the preservative from exposure. However, once the preservative is released to the environment, as for example by leaching, exposure to light can take place and photolytic chemical changes occur. Higher toxicities may result, since some pesticides form more toxic photoisomers when illuminated (Menzie 1972).

PERMANENCE

Besides loss of creosote from biodegradation at or near the surface, the problem of preservative leaching from the treated material arises. Thus Hockman (1967) in a summary report established that creosoted wood in a marine environment lost 30-40% of its preservative in the first year of service. He considered the hydration and swelling of the wood fibers to result in exudation of creosote and mechanical loss of the toxicant. Approximately two-thirds of the first year's loss occurred in the first month of exposure and the remaining one-third in the next 11 months. After the mechanical effects had disappeared, leaching still continued. *Limnoria* (crustaceans) and *Pseudomonas creosotensis*, along with other bacteria, colonize piles and apparently change the creosote characteristics; consequently the permanence of creosote is strongly dependent on conditions of exposure. Miller (1972) found similar losses (ca. 40%) in creosote retention for small specimens placed in circulating water in a laboratory over a 1-year period. In earlier work Sweeney et al. (1956) reported 40% loss of creosote from 1/8-inch pine panels after a year in sea water, and Colley and Burch (1961) noted 40-70% loss of creosote from 3/4-inch cubical pine blocks exposed for a year in coastal waters. Such large reported losses accompanied by more extensive use of coal-tar preservatives could conceivably develop into an environmental problem. This would become more acute if arsenic or 2% PCP were added to creosotes to increase their toxicity as proposed by Johanson (1969) and Leutritz (1964). But Miller (1972) is careful to point out that the rapid loss of creosote from small specimens is not observed for the larger pilings in an outdoor environment. Such findings emphasize the need for field studies of the depletion of preservatives and their fate in the environment.

CHLORINATED TOXICANTS AND PENTACHLOROPHENOL

Because of its cleanliness and resistance to leaching, pentachlorophenol and its water soluble sodium salt have been employed extensively as wood preservatives. In contrast to coal-tar creosote, PCP is a crystalline synthetic preservative and is highly chlorinated. It is stable, having low solubility and volatility. Employed as an oil-borne solution (5% PCP) to which waxes and resins may be added to prevent blooming, it at present has wide and satisfactory use. However, PCP has certain disadvantages when handled, since it is irritating to the skin and mucous membranes. For this reason protective clothing must be worn. PCP dissolved in liquefied petroleum gas, as in the Cellon process, apparently deposits in the cell wall of the wood, mainly in the middle lamella and S₂ layers and probably hydrogen-bonds with lignin of the wood (Resch and Arganbright 1971). A different deposition probably occurs with the more generally used PCP-in-oil process.

For some special applications chlorinated phenols other than PCP have been used. These include tetrachlorophenol, trichlorophenol and chloro-2-phenylphenol. Generally these substances have undesirable odors, are more volatile, and are more likely to cause skin irritation; they are also more water-soluble. In addition to these some metallosalts such as copper pentachlorophenate and zinc tetrachlorophenate have been tried as wood preservatives.

MICROBIOLOGICAL BREAKDOWN

In the concentrations used for wood preservative purposes, PCP may resist biodegradation in the ecosystem. However, some investigators claim that PCP can be completely degraded. Generally biodegradability is directly related to chemical structure. Resistance to breakdown with chlorinated aromatics is established by the position of the halogens on the aromatic nucleus, and the linkage of and type of aliphatic side chain (Alexander and Aleem 1961). Lyr (1963a) was one of the first to show that fungi, including some wood-rot fungi, were capable of detoxifying PCP; phenol oxidases, i.e. tyrosinase and peroxidase, were the enzymes. The stability of halophenols was found to increase with increasing chlorination of the aromatic ring. Detoxification occurred through inactivation of the hydroxyl group. Ingols and Stevenson (1963) also observed increased resistance to biodegradation with increased chlorination of the phenol ring. A partial depletion of PCP was noted in two investigations (Duncan and Deverall 1964, Unligil 1968) in which 43% of the original PCP was respectively lost, whereas almost complete depletion was claimed for the activity of *Trichoderma viride* and *Trichoderma virgatum* (Cserjesi 1967) acting on PCP. Apparently numerous species of bacteria and fungi are associated with material containing PCP (Cserjesi 1967, Petrenko 1969), but Petrenko (1971a, 1971b) concludes that the leading role in colonization of PCP-treated wood belongs to the bacteria, notably *Pseudomonas fluorescens*, *Bacillus cereus* and *Bacillus mycoides*. Microorganismal succession or the

sequential establishment of bacteria and fungi has been suggested as a cause of the depletion of PCP (Peterson et al. 1969). In contrast to this evidence for the biodegradation of PCP, Pauli and Franke (1972), while testing the compatibility of preservatives with sewage disposal microbiota, found that of the phenolic compounds tested, *o*-phenylphenol and chlorocresol showed rapid degradation, whereas PCP, trichlorophenol, and chloroxylenol were almost completely resistant during a 7-day test. Results were unchanged when incubation was extended to 14 days. Hexachlorophene was altered to an undetermined phenolic structure relatively resistant to further degradation. But a very recent study by Kirsch and Etzel (1973) concludes that PCP is metabolized. By using a mixed culture from soil conditioned to PCP over a 4-month period, reacting this with PCP- C^{14} (99.55% pure), and analyzing for CO_2 released as a result of metabolic oxidation, labelled $C^{14}O_2$ was recovered, amounting to nearly 70% of the labelled PCP used as substrate - and this over a 24-hour incubation period. Intermediate metabolic products were not determined.

From the foregoing, PCP would appear to be biodegradable by specific microorganisms. Under some conditions ring cleavage and degradation to CO_2 and water may occur. Alexander (1969) has stated that chlorinated-hydrocarbon insecticides are not metabolized to any significant extent by any soil species. Horvath (1972) believes that this view needs to be reconsidered in the light of findings for the cometabolic process. In a study of the biodegradation of the herbicide 2,3,6-trichlorobenzoate he has shown that this substance could be more readily broken down by the flora of lake water if Na benzoate (a probable intermediate) were added to the system. Similarly the utilization of alkyl benzene sulfonate by a *Pseudomonas* species was enhanced by the addition of phenol (Horvath and Koft 1972), as was the oxidation of chlorophenols by *Rhodotorula glutinis* (Walker 1973). Even glucose, a nonrelated analogue, can be used to enhance the degradation of chlorobenzoates (Horvath 1973). In these instances the principle of cometabolism is recognized as operative: the more easily metabolized cosubstrate supports growth of a greater population of active organisms equipped with an enzyme complement capable of degrading chlorinated aromatics. With this system, up to 100% degradation of aromatic material to CO_2 and water has been observed. Conceivably similar systems occur naturally in the global ecosystem. These would respond similarly to the introduction of toxic chemicals such as PCP to the environment.

DETOXIFICATION MECHANISMS

Investigation of the molecular changes that occur during biodegradation of PCP have been few. The chlorinated pesticides, such as DDT, lindane, methoxychlor, and heptachlor, have been more closely studied to determine their fate in the environment than has PCP. Menzie (1972) has recently reviewed the biodegradation and photolytic degeneration of pesticides. Apparently the main route for the aerobic microbial biodegradation of DDT (dichlorodiphenyltrichloroethane), a highly chlorinated aromatic substance, is by way of dechlorination to DDD, DDE, *p*-chlorobenzoic acid,

and other, unidentifiable, materials. Under anaerobic conditions DDD can be formed by reductive dechlorination. In a recent paper Sethunathan and Yoshida (1973) have shown that lindane, a heptachlorinated cyclohexane, is degraded anaerobically by a *Clostridium* species. When labelled carbon was used, neither labelled CO_2 nor CH_4 was collected, but radioactivity was lost, and this was indicative of breakdown of the lindane. Reacting chlorinated aliphatic acids with an enzyme system obtained from *Micrococcus denitrificans*, Bollag and Alexander (1971) showed beta but not alpha cleavage of chlorine and no evidence for the formation of 3-hydroxy acid intermediates during the dechlorination reaction. Helling et al. (1971) have reported that the introduction of the polar groups OH, NH_2 , $>\text{N}-\text{C}(\text{O})$, COOH , and NO_2 to chlorinated hydrocarbons often affords sites of attack. With more information of this kind it may ultimately be possible to tailor toxicants for specific targets and at the same time control their biodegradation in the environment. Persistence varies greatly with chemical structure, as shown by Chambers et al. (1963) in a study of 104 aromatic compounds and their response to a mixed bacterial culture adapted to phenol. Benzenes were oxidized with difficulty or not at all; dihydric phenols were oxidized, but trihydric phenols were not. Nitro- and chloronitrophenols were difficult to oxidize. The fate of halobenzenes in rabbits was studied by the St. Mary's Hospital medical school group, London (Jondorf et al. 1958, Parke and Williams 1960). Mono- and dichlorobenzene were detoxified to monochlorocatechol and dichlorophenol respectively. Trichlorobenzene was not readily utilized, but small amounts of corresponding phenols were detected with the less chlorinated substances. Interestingly enough the bacteria of the rabbit gut were considered the cause of the reactions.

The mechanisms for the depletion and detoxification of PCP have not been fully worked out. Rich and Horsfall (1954), in some early work employing the laccase system from two fungi imperfecti, found that phenols were oxidized to quinones and that the quinones were then polymerized to a nontoxic black pigment. Some time later, using phenol oxidase preparations and reacting them with PCP, Lyr (1962, 1963a) was able to detect chemical change in the PCP from a shift in its ultraviolet spectrum. Since no acid was produced, there was no ring cleavage. Detoxification appeared to occur by inactivation of the hydroxyl group. Hydrogen peroxide alone detoxified PCP (Lyr 1963b). Much later Hekmati and Bradley (1971) observed that organochlorine pesticides such as DDT and heptachlor epoxide were readily broken down by this reagent. From what was said earlier, under the detoxification of aromatics, it is generally accepted that dihydroxylation is a prerequisite to enzymatic fission of the benzene ring; apparently *cis*-glycol formation is also considered the pathway to detoxification of chlorinated aromatics (Gibson et al. 1968). In this investigation *Pseudomonas putida*, when grown with toluene as a carbon source, was found to oxidize chloro-, bromo-, iodo-, and fluorobenzenes to their respective 3-halogenated catechol derivatives. *Para*-chlorotoluene was oxidized to (+)-*cis*-4-chloro-2,3-dihydroxy-1-methylcyclohexa-4,6-diene, and 4-chloro-2,3-dihydroxy-1-methylbenzene, and the latter was demonstrated to have been produced from the former. In a study using a bacillus from soil which metabolized PCP, Suzuki and Nose (1971) observed that a major metabolite

pentachloroanisole and a minor metabolite tetrachlorohydroquinone dimethyl ether were produced.

In some earlier work (Engel et al. 1966) a musty taste in eggs and poultry was attributed to the presence of tetrachloroanisole associated in some way with the use of preservative-treated wood shavings as bedding. Subsequent study by Curtis et al. (1972) revealed that anisoles were formed by specific fungi acting on tetra- and pentachlorophenols present in the shavings as wood preservatives. In "simulated litter" experiments tetrachlorophenol was almost completely converted to the anisole in 9 days, whereas PCP was 50% converted to its anisole in 29 days. About the same time Cserjesi and Johnson (1972) found that *Trichoderma virgatum* grown in malt agar with PCP for 8 days reduced the PCP concentration to near zero. Only about 10 to 20% of the original PCP was recovered as pentachloroanisole (PCA). PCA, therefore, was not the only metabolite. These authors then asked if methylation is a first step in the biodegradation of PCP. In another investigation Cserjesi (1972) found that other species of *Trichoderma* and one species of *Penicillium* were able to methylate PCP to PCA. Total recovery as PCA was only found in two cases, but PCA was considered one of the main metabolites. In support of this, pentachloronitrobenzene (PCNB), a compound of similar structure and widely used for control of fungi, is reported to be metabolized to pentachloroaniline and to pentachlorothioanisole when exposed to the resistant fungus *Fusarium oxysporum* (Menzie 1972). Chacko et al. (1966) found eight species of fungi and eight actinomycete isolates able to attack PCNB. Pentachloroaniline was a metabolite. Activity in soil was considered to occur slowly, explaining the persistence of PCNB. Kaufman (1971) enlarged on this work and found that methylthiopentachlorophenol was formed from PCNB. Japanese workers (Konishi and Inoue 1972) considered that detoxification of PCP was caused by the laccase system of wood-rot organisms. By using the extracellular laccase from *Coriolus versicolor*, PCP was shown to be oxidized to quinoids, chloranil, and tetrachlorobenzoquinone-(1,2). Apparently these combine with PCP, yielding trichloro-(pentachlorophenoxy)-benzoquinone-(1,4) or dichloro-bis(pentachlorophenoxy)-benzoquinone-(1,2) as shown in Fig. 2. The detoxification pathway of PCP proposed here embodies an initial oxidation step followed by conjugation of the oxidized material through an ether linkage with existing PCP.

The mechanisms of the breakdown of PCP await further investigation. Meanwhile, it seems reasonable to assume that final detoxification pathways approaching those outlined by Ornston (1971) for aromatics and discussed earlier under the detoxification of aromatics can be expected. However, Walker (1973) has already found it puzzling that he failed to detect catechol formation in the reaction of chlorobenzoic acids with *Frodotorula glutinis*.

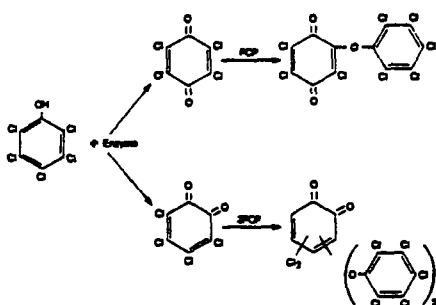


Figure 2. Probable detoxification of pentachlorophenol by the laccase of *C. versicolor*.

PHOTOCHEMICAL BREAKDOWN

In addition to biological degradation, PCP can undergo photochemical breakdown. For example, Crosby and Hamadmad (1971) showed that PCP, PCNB, and pentachlorobenzene underwent reductive dechlorination in ultraviolet light at 253.7nm. Free radical formation or hydride transfer was suggested as the possible mechanisms. However, in sunlight these compounds were unchanged, and in the authors' view photolytic degradation is not significant. On the other hand, photochemical degradation of Na-PCP was studied extensively in Japan, where this substance is used as a herbicide (Cserjesi 1972). Photodegradation products were formed by condensation reactions. A number of these degradation products were found to be stronger fungicides. Similarly, ultraviolet decomposition of the insecticide lindane evidently resulted in formation of photoisomers more toxic to flies and mosquitoes than the initial compound (Menzie 1972). It is thus common for a biocide passing through the environment to become more toxic because of a rearrangement of its molecular structure. Crosby and Li (1969) have indicated that practically all herbicides are capable of photodecomposition and consider the products produced to be similar to those for biological and chemical decay. This fact is not generally appreciated and calls for a more careful evaluation of the photodecomposition reactions of fungicides. Some basic work by Kuwahara et al. (1969, 1970) on the decomposition of PCP by sunlight has shown 40 to 60% conversion to a complex colored tar and other products after irradiation for a 2-week period. These products result from the formation of pentachlorophenoxy radicals and hydroxy radicals that condense to produce, for example, 2,5 dichloro-3-hydroxy-6-pentachlorophenoxy-*p*-benzoquinone, 3,4,5-trichloro-6-(2 hydroxy-3,4,5,6-tetrachlorophenoxy)-*o*-benzoquinone, other variously colored ethers, and tetrachlororesorcinol. In general, all had lower fungicidal activity and lower fish toxicity than PCP, but some had the same or greater activity against specific microorganisms. Apparently many aromatics including phenols and cresols are photooxidized by sunlight (Crosby 1972). Fortunately, wood preservatives such as PCP are protected from exposure, as they are used below ground and by strong complex formations with the wood.

PERMANENCE

In general PCP does not leach, especially if applied by oil carrier. Permanence is related to the low solubility of PCP in water. No extensive study of the fixation of this preservative in wood has been made, and this in itself shows that little leaching occurs. However, Unligil (1968) has shown that PCP was removed from blocks of treated wood during steam sterilization. Similar but long-term leaching can probably be expected for soil and water exposures under outdoor hot humid cyclical weather conditions.

There is some question concerning the permanence of PCP in wood treated by the Cellon process, in which the carrier is liquefied petroleum gas (LPG). Recovery of the LPG during treatment practice may affect PCP distribution and fixation and result in more leachability.

The current practice of incorporating water-repellent waxes and oils with carriers to prevent blooming (blooming causes loss of PCP) undoubtedly reduces the rate of water absorption in the treated material. The reduced mechanical working of the wood may contribute to greater permanence of PCP under conditions of service.

METALLORGANIC AND INORGANIC WOOD PRESERVATIVES

Water-borne metal-salt preservatives are increasingly useful in the wood preservation industry because of their biological effectiveness, permanence, and compatibility with painting and gluing. With the addition of water repellents to the preservatives, the wood becomes dimensionally stable and water repellent. Copper chrome arsenate (CCA), a wood preservative of this group, is considered one of the most versatile available. However, copper naphthenate in oil, copper pentachlorophenate, organic tin compounds, phenylmercuric acetate, bifluorides, borates, and quaternary ammonium compounds are also employed in specific circumstances. Nitrogen and phosphate have been added to these formulations and more recently formaldehyde, melamine, dicyandiamide, and phosphoric acid mixtures have been tried as fire retardants (Juneja 1972).

The application of metallic compounds as wood preservatives generally results in a strong binding of the inorganic materials with the wood and the formation of ill-defined complexes. These complexes become sites active against biological decay and concomitantly sites for the breakdown of the preservatives. Wood preservative metallorganic compounds, as for example copper naphthenate, bi- and trialkyl tin, and zinc carbamate, also form complexes with wood. The physicochemical nature of these complexes is still very much an open question. Bayley and Rose (1960) claim that copper is bound by the acidic groups of the noncellulosic constituents of the wood, whereas Bland (1963) considers that the primary wall and intercellular layer, namely the lignin, sorbs copper and that a reaction mechanism apart from that with uronic acid carboxyl groups effects most of the complexing.

The chromium ion of CCA is considered to influence the permanence of these formulations, but here also the mechanism is not clear (Wallace 1968). More recently Dahlgren (1972) has claimed that CCA in contact with wood results in an increased acidity because of ion-exchange and adsorptive reactions with the wood. During the precipitation of the active elements the acidity continuously decreases until all the chromium is consumed. Early-reaction products are reported to be unstable, but stable ion-exchange fixation products finally result and react with the wood. Electron microscopic study of CCA-impregnated wood (Chou et al. 1973) has shown that all three toxic elements of the preservative are located within the cell wall including the middle lamella. The lumen is well covered also. Whatever the toxicant-to-wood complexing mechanisms with water-borne preservatives, fixation is not so great that leaching and preservative loss to the environment cannot occur.

MICROBIOLOGICAL BREAKDOWN

Inorganics and metallorganics used as wood preservatives should be considered biodegradable just as were the organic wood preservatives already discussed. This is to be expected since, even from the beginnings of serious microbiological investigation, organisms have been known that derive their energy requirements by oxidation and reduction of inorganic substances. In later studies microbiological reactions for many inorganic compounds have been reported. In a survey of microbial reactions with inorganics, Silverman and Ehrlich (1964) have drawn up an extensive list (not claimed to be complete) of oxidation and reduction reactions for inorganic ions. Included are reactions for As, Cu, Cd, Se, Zn, P, and S. Two general reactions are operative for transformation of inorganic substances. In the one autotrophic organisms make use of inorganic substrates to derive their entire energy requirements, whereas in the other, heterotrophic organisms effect elemental ionic changes but derive most of their energy requirements from metabolizing organic material concomitantly (Alexander 1971). In a recent paper (Bautista and Alexander 1972) many inorganic substances in the oxidized state, arsenate included, were shown to be readily reduced by *Micrococcus* and other species, and by cell-free enzymic preparations as well. Under anaerobic conditions microorganisms are known that obtain their oxygen requirements from inorganic oxides. The best-known example is the denitrification of nitrate to molecular nitrogen by many microorganisms, a phenomenon that helps maintain the nitrogen equilibrium of the ecosystem. Apparently reductive capacity is common to many soil microorganisms.

Duncan and Deverall (1964) have reviewed the early work on the inactivation of toxicants used as wood preservatives and point out that, in addition to other reactions, arsenic can be transformed to trimethylarsine, a gas, by fungal action. Thom and Raper (1932) showed that numerous gaseous-arsenic producers could be found among the then known organisms and that arsenic-tolerant types were numerous in soil. Many mold fungi colonizing pine fence-posts were tolerant to high concentrations of several salt

preservatives (Duncan 1960). In a study of treated fence posts (Madhosingh 1961), the ubiquitous soil saprophyte *Fusarium oxysporum* was suggested as in some way capable of reducing the toxicity of fluor-chrome-arsenate-diphenol, a wood preservative mixture, and thereby enabling subsequent colonization by *Coprinus micaceus*. Wood blocks treated with copper arsenate, and fluoro-chrome-arsenate-dinitrophenol, when exposed to various fungi associated with wood-rot but not capable of producing it, subsequently became much more susceptible to decay by typical wood-destroying fungi. This suggested that these preservatives were in some way modified or depleted by the initial fungal activity. In a study of the colonization of metallic salt and CCA-treated wood (low retention values) with ground exposure, Butcher (1971) noted a succession of fungal species beginning with molds and progressing to soft rot, to secondary molds, and to primary basidiomycetes (white rots). Dominant species were *Penicillium*, *Cladosporium*, *Fusarium*, *Trichoderma* and *Cephalosporium*, and these were considered tolerant of CCA preservatives. Levi (1969) noted that strains of *Poria vaillantii* and *Merulius himantioides* were tolerant to copper sulfate and arsenic pentoxide. Da Costa (1959) also observed a high tolerance of a *Poria vaillantii* strain to copper, zinc arsenic, and a CCA formulation. Greaves (1968) has suggested that CCA treatment may enhance bacterial colonization of wood exposed as in cooling towers by reducing the growth of competitors - the fungi. In a later study with ground stakes Greaves (1972) found that CCA treatment had no significant effect upon the diversity of organisms that colonized the wood. *Penicillia* predominated and with exposure actinomycete colonization increased. Bacteria colonized the wood early and included *Bacillus*, *Pseudomonas*, *Flavobacteria*, and *Serratia* species. All these observations suggest that inorganic preservatives are susceptible to varied microbiological activity.

DETOXIFICATION MECHANISMS

Of inorganic preservatives, the mechanisms for detoxification of mercurial toxicants have been most closely studied. It is generally agreed that in aquatic environments inorganic mercury is methylated to methylmercury. Experimental support for this was furnished by Jensen and Jernelov (1969) when they showed that inorganic mercury was converted to monomethyl- and dimethylmercury in aquarium sediments. Methylmercury, which has a very strong affinity for organic matter, was found to accumulate in fish and these, as a part of the dietary food chain, transferred it to higher animals and man. Dimethylmercury is volatile and can escape to the atmosphere, where ultraviolet irradiation can convert it to metallic mercury (Langley 1973). Spangler et al. (1973a) pointed out that two types of methylation are possible, the one enzymatic via an organism such as *Clostridium cochlearium*, the other chemical via methylcoalbumin (produced by methanogenic bacteria), which under laboratory conditions at least, methylates Hg^{2+} . Methylmercury is degraded also, and Spangler et al. (1973b) were able to isolate 30 bacterial strains capable of biodegrading it from environmental sources. Both aerobic and facultative anaerobic types were found, some with characteristics of typical pseudomonads. Degradation is by reductive demethylation

resulting in the formation of methane and inorganic mercury and occurs under aerobic and anaerobic conditions.

Mercurial compounds were used for early wood preservation treatments, and phenylmercuric acetate (PMA) has had some use in the storage of pulp. Russel (1955) and Kiessling (1961), among other investigators, have observed that large amounts of PMA are adsorbed by *Penicillium roquefortii*. This is apparently caused by the affinity of PMA for sulfhydryl groups of mycelial protein. This adsorption can result in the "biomagnification" phenomenon (Johnson and Kennedy 1973), whereby microorganisms act as physical agents in accumulation and movement of pollutants from aquatic ecosystems. Greenaway (1971) noted that isolates of *Pyrenopeziza avenae* in the presence of PMA secreted pigments and that a close correlation existed between pigment production and resistance to PMA. A solution containing pigment was able to remove phenyl Hg^+ (ions) from aqueous solution. The suggested mechanism involved is a chelation of ions by anthraquinone. Working with microorganisms isolated from lake-bottom sediments and soils Matsumura et al. (1971) have shown that PMA is metabolized quickly. One major metabolite was diphenyl mercury. Methyl mercury, although expected, since it is often observed when inorganic mercurials biodegrade, was not found. Nelson et al. (1973) observed that mercury-resistant bacteria, predominately *Pseudomonas* species, from water and sediment, converted PMA to gaseous mercury (Hg^0) and benzene. It is noteworthy that some mercurial metabolites are strongly affected by light. For example, Fuse and Nishimoto (1963) have shown that ethyl mercurials containing various anions exhibited decreased fungicidal activity after exposure to light. The effect was found dependent upon the anions present. In contrast aryl mercurials such as phenylmercuric chloride oleate showed no photodegradation.

Alkylation, namely methylation, as a mechanism for detoxification, has already been noted in this discussion. In addition to mercurial and arsenious compounds other inorganics are detoxified by alkylation. *Scopulariopsis brevicaulis* converted sodium methyl arsenate and various alkylarsonic acids to alkyl dimethylarsines, but selenite and tellurite were also alkylated to dimethyl selenide and telluride respectively (Challenger 1945a, 1945b). The element sulfur was not affected except in the form of alkyl or dialkyl sulfides, in which case the corresponding mercaptan and methyl alkyl sulfide were formed. Fleming and Alexander (1972) observed also that selenium and tellurium were methylated, but by a *Penicillium* isolate from raw sewage. Although methylation may be an important mechanism of detoxification (apparently it is the major mechanism for selenium detoxification in the rat), Fleming and Alexander conclude that alkylation is not a significant mechanism of selenium detoxification with the particular microorganism used. However, new alkyl derivative toxicants may be formed by this mechanism. Indeed, alkyl tin compounds have been tried as wood preservatives. These, as well as phenyl tin compounds, have shown impressive toxicities with respect to wood-rot fungi (Hof 1969, Richardson 1970). For example, tri-n-butyltin oxide, tri-n-butyltin acetate, and triphenyltin acetate were found highly toxic to *Contiophora puteana*, but their toxicities to insects were less impressive. Trisubstitution apparently provides the stronger biocide.

Detoxification by precipitation of the toxicant has been observed. Copper contributes in part to the total toxicity of CCA formulations. In early studies into wood preservatives Rabanus (1939), after observing tolerance to copper by certain fungi in treated poles, suggested that tolerance might be linked with the formation of insoluble copper oxalate formed from oxalic acid produced by the fungi. In one instance copper was observed to be taken up by mycelial substance (Truckenbrodt 1962), an effect enhanced by alkaline conditions that also gave rise to the formation of giant cells. Copper oxalate crystal formation was noted during growth of *Seriolellus palustris* (Ishii and Kawamura 1967) and *Poria monticola* (Levi 1969) in synthetic media containing copper sulfate. In the latter case *Poria vaillantii* growth caused the precipitation of copper but apparently as the sulfide. Similar results were obtained with yeast cells (Ashida et al. 1963) and copper tolerance was attributed to the formation of H_2S . Copper sulfide was found deposited in the cell walls, but there was no evidence that H_2S diffused from the cells to precipitate copper sulfide in the medium. Copper oxalate formation is more generally observed by investigators, and Levi (1969) has shown that it is much less toxic to wood-rot fungi including the copper-tolerant *Poria* species.

Depletion of preservative is contingent upon acidity. Levi (1969) showed the importance of culture acidity by exposing CCA-treated sawdust to the culture supernatants of a number of wood-rot organisms. High percentages of Cu, As, and Cr were leached from the wood after such treatment. Generally the proportion of the component removed increased as the acidity of the culture filtrate increased. This is in agreement with the findings of Horsfall (1956) and Young (1961) and suggests that, no matter what the source causing acidity, removal of inorganic ions is facilitated. Soil, water, and atmospheric conditions can also produce an acidic environment or a situation leading to loss of preservative. For example, wood treated with preservatives based on fluoride was found to lose 50-80% of its fluoride content merely upon standing in a loft. The action was attributed to diffusion and volatilization phenomena (Becker and Berghoff 1968), but the atmospheric conditions may have been the prime factor.

PERMANENCE

In spite of the detoxification and depletion phenomena already noted, a good degree of permanence for water-borne preservatives is to be expected. The use of multisalt as opposed to unisalt preservatives has resulted in stable preparations resistant to leaching. Chromium-copper (CC) and CCA preparations have proved themselves, particularly in arduous cooling-tower tests (Belford 1970). If fluoride and boron are included in these formulations, high leachability can be expected, reaching as much as 90% for boron. As Belford states, little effort has been made to isolate the factors contributing to permanence, and it is difficult to interpret laboratory data for service use. The usefulness of laboratory findings is also questioned in an earlier paper (Price and Watson 1962) and both publications express the need for more field testing. The authors of the latter paper expect that CCA preservatives entirely resistant to leaching

will eventually be developed. As evidence of the worth of CCA treatment, they note the Bell telephone-pole data for North America, where one quarter of a million poles (vacuum- and pressure-treated) have stood completely trouble-free up to 22 years. Laboratory tests regularly show a high incidence of leaching; field tests show less (Wallace 1968). Leachability in service therefore may not be as extensive as laboratory data at times indicate. However, the interrelationship of the ecosystem and the treated material may markedly affect leachability as biodegradation and detoxification mechanisms become operative.

ENVIRONMENTAL HAZARDS OF TOXIC CHEMICALS AND WOOD PRESERVATIVES

Highly chlorinated molecules at present used as herbicides and insecticides have already been singled out as detrimental and hazardous to the environment. Risebrough et al. (1968) have discussed the declining population of fish-eating birds in Great Britain and North America and identify this with the wide dispersal of polychlorinated biphenyls and DDT-like substances in the global ecosystem. Evidently body lipids solubilize chlorinated pesticides with subsequent effect on the reproductive cycle and the calcium metabolism. This ultimately results in the production of fragile, thin-shelled eggs, and these are destroyed before they can be hatched. Residues of DDT have also been implicated in the reproductive failure of fish. DDT stored by fish is transferred to the roe and appears in the yolk sac after hatching, causing the death of the young fish (Menzie 1972).

The situation for wood preservatives is more fortunate. No extensive environmental disturbance or health hazard has arisen from the present use of the better-known wood preservatives, creosote and PCP. Only in isolated instances have there been difficulties. For example, Kadlec et al. (1962) have reported that plant personnel handling hot creosote developed occupational skin diseases ranging from eczema to carcinoma. Rummeler (1961) reported his experiences with wood preservatives and domestic animals and has recommended that only approved preservatives be used for protection of farm buildings. Creosotes (coal tar and brown tar) were not among those recommended. Similarly Schipper (1961) observed that creosote and PCP were toxic to swine. In 1970 Ohio suffered a massive fish kill (1.8 million) attributed to leakage of PCP from a storage tank. Similarly there were two cases in Texas, where a smaller number of fish were killed: again toxicity was attributed to PCP, in one instance from failure to close a valve, in the other from a leak in a tank. These problems occurred because of process failures not *via* waste water discharge (Adams 1970). It is of considerable interest that Kirsch and Etzel (1973) (see Arsenault 1973) have developed a method for treating the effluents of plants handling PCP, using an organism they have isolated that can metabolize PCP completely to carbon dioxide and water. Thus PCP is completely degraded by specific organisms of the ecosystem. On the other hand, recent developments in the oil industry have caused a scarcity of petroleum-based chemicals including phenols. This may retard the use of PCP and thus the possibility of its ever becoming a major environmental pollutant.

Inorganic toxicants are being used increasingly for the preservation of wood. Mercury-containing substances have been used successfully in the past as fungicides but have polluted the environment and created a health hazard. For example a large number of Japanese fishing folk were seriously poisoned at Minamata Bay (Irukayama 1967). The trouble was traced to the effluent of a large chemical plant that contained methylmercuric chloride. Similarly, when certain bird populations drastically decreased in Sweden (Borg et al. 1966), poisoning was finally correlated with unusually high concentrations of mercury in dead birds (Rosen et al. 1966). Alkyl mercurials are excellent fungicides, but the methyl and ethyl mercurials are known to cause brain damage, and kidney lesions result from aryl mercury poisoning. Alkyl tin salts effectively inhibit oxidative processes; but, unlike the damage caused by mercurials, tissue damage is reparable and the oxides are harmless. In contrast to mercurials, little used for the preservation of wood, inorganic preservatives can generally claim a long history of safe use (Barnes 1970), a fact probably attributable to proper treatment practice and usage. No major complaint has been registered against CCA or the individual chemical elements comprising it. Arsenic in the pentavalent form has had wide use in agriculture without protest. Borates have also been used safely. Only in isolated instances has the use of inorganic preservatives been questioned. For example, Lohwag (1961) reported the lethal poisoning of several cows from wood preservatives that contained fluorine, chromium, and arsenic: after treatment the residue was discarded carelessly and the animals imbibed it. Cod and char fillets in contact with CCA-treated wood of fishing vessels were found to take up arsenic (Pedersen 1966), but the quantity was not considered dangerous. Behrbohm (1961) has discussed the toxic hazards for humans of wood preservatives containing chromates. These seemingly caused numerous cases of eczema, and their inhalation was suggested as causing lung cancer.

The main environmental problem the wood-preservation industry will have to face is the disposal of treating plant effluents and pollution from accidental leakage of storage and treating tanks. Fortunately much of the technology for countering these problems is at present available and is probably best handled by a lagoon disposal system. Dust and Thompson (1973) have conducted pilot-plant and bench-scale studies of the biological treatment of effluents from the wood-preserving industry from this standpoint. Removal efficiencies in excess of 90% were claimed.

Possibly no conflict will ever arise between environmental programming and the wood-preservation industry, especially if good treatment practice is followed, operations are clean, and nonleachable preservatives are selected where extensive usage is envisaged. If conflict should occur, decision-making could be based on the experience gained from the history of DDT, ably discussed by Borlaug (1971). In this situation, although heavy occupational exposure of hundreds of millions of people to DDT had occurred, very few cases of injury were reported and most of these were from malpractice, yet the product was revoked. Recently a correspondent for *Nature* (Anon. 1973), while covering the proceedings of the Pesticides Group of the Society of Chemical Industry, restated the statistics for the appalling increase of malaria in Ceylon since the stopping of DDT spraying for so-called economic reasons. The chairman of the group stressed that

safety depends on the care with which pesticide products are handled and applied. More training of operators and better publicity regarding the safety steps that industry is taking were suggested to ensure continued use of effective toxicants.

PROSPECTS FOR NEW WOOD PRESERVATIVES

Increased widespread use of wood preservatives may evoke development of so-called "soft" types, which are biodegradable upon entering the environmental ecosystem. Some difference of opinion exists as to whether pesticides that include fungicides can be designed to degrade rapidly under environmental conditions and still selectively control target organisms. Kearney and Plimmer (1971) doubt the possibility of achieving this. In contrast Kaufman et al. (1971) believe it can be accomplished. Willeitner (1973) considers the contribution of wood preservatives as a pollution hazard to be negligible but still thinks it essential that less pollutive reagents be developed and maintains that the wood preservative industry is already doing this.

Antibiotic toxicants perhaps offer possibilities in the search for new preservatives. For example, Stillwell et al. (1973) have described the isolation and production of scytalidin, a metabolite of *Scytalidium* species. Some 52 fungal species were found to be inhibited by this antibiotic, and it has been shown to be active against many fungi associated with the stain and decay of pulpwood chips in outside storage. This compound is suggested as a possible replacement for existing chemicals used for this purpose but which threaten the environment.

Schultz and Matz (1973) have described two types of microbiocides that are biodegradable but active against slime-forming molds. One is an n-alkyl aliphatic diamine containing 8 to 18 carbon atoms with short-chain organic acids added to produce water solubility. The other employs derivatives of trialkylbenzylammonium chloride, in which one n-alkyl contains 12 to 18 carbon atoms, and the others one or two carbon atoms. When discussing microbial degradation of toxicants in soil, Helling et al. (1971) have pointed out that the introduction of polar groups in chlorinated hydrocarbons often affords sites for biodegradation. New preservatives might be designed around such molecular structures by employing suitable polar groups.

New preservatives may also be found by keeping a close watch on the development of new pesticides for agricultural use. As a result of close cooperation between crop protection research and paint technology, several fungicides have come to be used as paint fungicides (Pauli 1972). These include Folpet (N[trichloromethylthio]phthalimide), Fluorofolpet (N-[fluorodichloromethylthio]phthalimide), which is more effective, Dichlofluanid (N-dimethyl-N'-phenyl-N'-[fluorodichloromethylthiosulfamide]), and Dow SA1013 (tetrachloropyridine-4-methylsulfone). These toxicants have proved effective against the few fungal species recognized as causing paint film deterioration; but, along with forthcoming fungicides, they may be found effective against a wider spectrum of organisms and replace some of the highly toxic preservatives at present used.

Biological control - employment of biological antagonists - is a feasible alternative to the use of toxic chemicals for prevention of wood decay. The application of biological agents for control has been suggested as one of the most promising ways of gradually replacing toxic pesticides now used in agriculture (Conservation Foundation 1969). In keeping with this the U.S. Department of Agriculture has shifted a major portion of its research funds from chemical studies to investigation of biological control methods. Employment of biological controls for prevention of wood decay is not new. In some early work, wood infected with bacteria was shown to be resistant to wood rot (Tichy 1953). Later Rada and Rypacek (1954) and Shields and Atwell (1963) reported that colonization of wood by *Trichoderma viride* increased its resistance to attack by wood decay organisms. Antibiosis and mycoparasitism have both been considered as the basic mechanisms contributing to this type of preservation, but recently Hulme and Shields (1970, 1972) have presented data that favor competition for simple nutrients as giving resistance to decay. Future study in this area will decide whether biological control methods can suitably replace toxic chemicals. Some experts believe that an integrated control program, making maximum use of biological and cultural methods coupled with the necessary application of toxic chemicals, will minimize pollution with pesticides (Conservation Foundation 1969). For some wood preservative applications a similar integrated program may also reduce the hazard of environmental pollution.

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